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(54) METHOD FOR MANUFACTURING RUBBER COMPRISING PRECIPITATED SILICIC ACID

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing a master batch of precipitated silicic acid with the silicic acid being well dispersed in the master match.

SOLUTION: In the manufacturing method, the master batch of precipitated silicic acid is obtained by blending a rubber latex with the silicic acid in a state of solution, followed by aggregation of both materials, washing with water, dehydration and drying. The silicic acid used has an average particle size of $\leq 1 \mu\text{m}$.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the precipitate silicic acid masterbatch characterized by mixing a rubber latex and precipitate silicic acid in the state of a solution, and using the precipitate silicic acid whose mean particle diameter it is the manufacture approach of after [mixing] co-coagulation, and the precipitate silicic acid masterbatch rinsed, dehydrated and dried, and is 1 micrometer or less as this precipitate silicic acid.

[Claim 2] The manufacture approach of the precipitate silicic acid masterbatch according to claim 1 which is precipitate silicic acid to which surface preparation of the precipitate silicic acid was carried out by cationic resin.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a precipitate silicic acid masterbatch. The manufacture approach of the precipitate silicic acid masterbatch for manufacturing in detail rubber, such as SBR which precipitate silicic acid contained, simple is offered.

[0002]

[Description of the Prior Art] Precipitate silicic acid has been used more widely as a bulking agent of rubber than before. When blending precipitate silicic acid with rubber, the approach of generally blending into rubber using kneading machines, such as Banbury, an opening roll, and a kneader, is performed widely. However, since precipitate silicic acid has a silanol group on the front face and has strong autoagglutination nature in it, it is difficult for it to make it distribute in rubber easily.

[0003] Therefore, although amelioration of the various kneading approaches etc. is performed, the present condition is that the still suitable solution approach is not found out.

[0004] the carbon black for which precipitate silicic acid is widely used with precipitate silicic acid as a bulking agent for rubber as described above -- comparing -- scouring -- ** and others -- the lowness of productivity is conspicuous. Therefore, since the reinforcement nature and workability were surely inferior as a reinforcing filler of rubber compared with the time of using carbon black, precipitate silicic acid was used as a complement agent of carbon black in many cases.

[0005] On the other hand, precipitate silicic acid attracts attention as a bulking agent for tires for passenger cars instead of carbon black in recent years for the purpose of coexistence of fuel consumption nature and grip nature. However, for the badness of dispersibility which was described above, and productivity, the loadings which demonstrate the greatest effectiveness cannot be added but the evil in which only combination which pressed down loadings to aforementioned one half extent can be performed is pointed out.

[0006] Moreover, although it is also examined for the purpose of wear-resistant improvement and improvement in driving stability that specific surface area uses 300m precipitate silicic acid of the small particle diameter it is [particle diameter] about 2/g, the autoagglutination nature of precipitate silicic acid has further increase, and workability and the problem of causing wear-resistant aggravation, on the contrary as it becomes small particle diameter.

[0007] That is, when the precipitate silicic acid of the above-mentioned small particle diameter is used, the Mooney viscosity when kneading to rubber increases, workability gets worse, or distribution worsens, and the evil of abrasion resistance getting worse on the contrary arises. Therefore, the present condition is that the limit is added also to the design of the physical properties of precipitate silicic acid itself.

[0008] The idea of making the masterbatch with which precipitate silicic acid or carbon black is blended at the time of rubber manufacture, and the bulking agent is blended beforehand is proposed for many years, and the above-mentioned masterbatch is already marketed about carbon black in order to solve the above-mentioned problem, for example, as indicated by JP,36-19390,B.

[0009] Co-coagulation is carried out, after carrying out mixed distribution of a rubber latex, and an oil emulsion and carbon black by the suitable ratio and mixing both dispersion liquid as the manufacture approach of the above-mentioned masterbatch. Then, after rinsing a co-coagulated substance and removing an impurity, the method of obtaining a carbon black content masterbatch is adopted by dehydrating, taking out the solid content which dehydrated and drying.

[0010] The precipitate silicic acid content masterbatch which applied the above-mentioned approach has still come [however,] to be marketed. This reason originates in the autoagglutination nature and the hydrophilic property which the above mentioned precipitate silicic acid has. That is, after mixing dispersion liquid, even if it carries out co-coagulation like the above-mentioned approach in the case of precipitate silicic acid, it will originate in autoagglutination nature and a hydrophilic property, and precipitate silicic acid will not be enough incorporated in a rubber latex, but precipitate silicic acid and a rubber latex will carry out separation precipitate separately. As a result, if it rinses in the condition, almost all precipitate silicic acid is washed out, in rubber, most precipitate silicic acid is not blended and the target masterbatch cannot be obtained.

[0011] Moreover, the manufacture approach of the precipitate silicic acid masterbatch by making a rubber material science introduction (Japanese BAL car industrial-stock type *****: Heisei 7 issue) compound precipitate silicic acid in a rubber latex is proposed.

[0012] However, there is a problem that the amount of the precipitate silicic acid which can be blended into rubber also by the above-mentioned approach has only one half extent of the amount which demonstrates the greatest effectiveness, and further, at the reaction in a rubber latex, since it is difficult to control many physical properties, such as specific surface area of precipitate silicic acid, and oil absorption, it has the fault that many physical properties of precipitate silicic acid are limited.

[0013]

[The technical problem which a problem tends to solve] Therefore, even if it blended into rubber the amount which demonstrates the greatest effectiveness, a method of manufacturing easily the fully distributed precipitate silicic acid content rubber was desired.

[0014]

[Means for Solving the Problem] Then, this invention person etc. repeated research wholeheartedly about the approach of manufacturing the precipitate silicic acid masterbatch which the precipitate silicic acid blended in large quantities in the rubber latex distributed good.

[0015] Consequently, when mean particle diameter carries out mixed distribution of this precipitate silicic acid and the rubber latex in a solution using precipitate silicic acid 1 micrometer or less After mixing, when carrying out co-coagulation, acting as Mr. [coprecipitation], without carrying out separation precipitate finds out that the precipitate silicic acid masterbatch by which precipitate silicic acid is distributed good in rubber by performing rinsing and dehydration / desiccation actuation is obtained in a header and this precipitate, and it came to complete this invention.

[0016] That is, this invention mixes a rubber latex and precipitate silicic acid in the state of a solution, and it is the manufacture approach of after [mixing] co-coagulation, and the precipitate silicic acid masterbatch rinsed, dehydrated and dried, and it is the manufacture approach of the precipitate silicic acid masterbatch characterized by using the precipitate silicic acid whose mean particle diameter is 1 micrometer or less as this precipitate silicic acid.

[0017]

[Embodiment of the Invention] If mean particle diameter is 1 micrometer or less, what kind of precipitate silicic acid may be used for the precipitate silicic acid used in this invention, and the precipitate silicic acid whose mean particle diameter is 50-500nm especially is suitable for it in this invention. In addition, in this invention, mean particle diameter is a volume criteria median diameter when measuring with the particle-size-distribution plan of a light-scattering diffraction type.

[0018] Moreover, the precipitate silicic acid used in this invention takes into consideration the purpose which it is not restricted at all and needed about the physical properties and the manufacture approach, and should just determine it suitably.

[0019] For example, if it takes into consideration using as a bulking agent for rubber as physical

properties of precipitate silicic acid, that whose specific surface area is 50-350m²/g is suitable, and that whose oil absorption is 100-300 cc / 100g suitable.

[0020] Moreover, what is necessary is just to determine suitably also about pH of the above-mentioned precipitate silicic acid, and the amount of impurities according to the purpose. For example, the precipitate silicic acid which added metal salts, such as aluminum and magnesium, can also be used during manufacture of precipitate silicic acid, or after manufacture, a metal salt can be added in an aging process, and the precipitate silicic acid which performed surface treatment with the metal salt can also be used satisfactory at all.

[0021] As the above-mentioned amount of impurities, if the effectiveness of this invention is taken into consideration, it is suitable that it is 3% or less of precipitate silicic acid. As long as it is the within the limits, the property of the rubber obtained may be taken into consideration and you may set up suitably.

[0022] Furthermore, surface treatment may be performed by the well-known finishing agent in the range which does not check the effectiveness of this invention. If the distribution in rubber is taken into consideration also in it, it is suitable to carry out surface treatment by cationic resin.

[0023] If it is the oligomer or the polymer which dissociates as the above-mentioned cationic resin when it dissolves in water, and presents cationicity, it can use without being restricted especially and the oligomer or the polymer which has the 1st - tertiary amine, or quarternary ammonium salt especially can use suitably. For example, what introduced the amine radical and the quarternary-ammonium-salt radical into water-soluble nature or synthetic macromolecule may be used, and homopolymerization, the copolymerized water-soluble oligomer, or a polymer may be used for the monomer which has an amine radical and a quarternary-ammonium-salt radical. It is suitable to use homopolymerization, the copolymerized water-soluble oligomer, or a polymer for the monomer which has quarternary ammonium salt also in it.

[0024] As an amount in the case of carrying out surface treatment by cationic resin, 3 - 30 weight section is suitable to the precipitate silicic acid 100 weight section, and 5 - 15 weight section is more suitable. That is, without carrying out separation precipitate by making it the above-mentioned range, the dispersibility to rubber becomes good and a lot of combination of it is attained.

[0025] The manufacture approach of the precipitate silicic acid used for this invention is not limited especially, either, and, generally the approach of depositing in a water solution is adopted by counteracting silicate of soda and acids, such as a sulfuric acid. Moreover, in order to manufacture the precipitate silicic acid containing many metal salts, you may make it counteract by using an aluminum sulfate instead of [all] some above-mentioned acids [at least].

[0026] Moreover, after the above-mentioned neutralization, although what passed through filtration, washing, and a desiccation process may be used, in this invention, it is suitable to use the thing of the silica slurry regime which does not pass through the above-mentioned desiccation process. That is, by not passing through a desiccation process, since the drying shrinkage at the time of increase and desiccation does not produce a degree of freedom more, the physical-properties design of precipitate silicic acid becomes advantageous also in respect of cost.

[0027] The approach of manufacturing the precipitate silicic acid with a mean particle diameter of 1 micrometer or less used in this invention does not have especially a limit, either. For example Although the method of manufacturing the approach of controlling a reaction condition etc. and manufacturing precipitate silicic acid with a mean particle diameter of 1 micrometer or less in case the above-mentioned precipitate silicic acid is manufactured, and, beforehand larger precipitate silicic acid than the target mean particle diameter, and manufacturing precipitate silicic acid with a mean particle diameter of 1 micrometer or less by subsequently grinding etc. is mentioned The method of manufacturing larger precipitate silicic acid than the target mean particle diameter beforehand, and manufacturing precipitate silicic acid with a mean particle diameter of 1 micrometer or less by subsequently grinding also in it, from the point of the dispersibility to rubber and the ease of carrying out of control of mean particle diameter, is suitable.

[0028] it restricts especially as the above-mentioned approach of pulverizing -- not having -- a well-known approach -- grinding -- ****ing -- for example, the shape of fine particles and a cake, although

the approach of grinding the precipitate silicic acid of the shape of a ** or a slurry with well-known grinding equipment is mentioned. The approach of pulverizing with grinding equipments, such as DISUPA, a homogenizer, and a colloid mill, also in it using the precipitate silicic acid (henceforth a silica slurry) of the slurry regime which will not pass through the above mentioned desiccation process if the dispersibility to rubber, the ease of carrying out of actuation, etc. are taken into consideration is suitable.

[0029] Although especially the original mean particle diameter of the precipitate silicic acid in the above-mentioned case of grinding is not limited, it is suitable for it that it is 10-30 micrometers. Moreover, what is necessary is not to restrict especially grinding conditions, either, but just to set up conditions suitably so that it may be set to 1 micrometer or less. For example, when a homogenizer is used, precipitate silicic acid 1 micrometer or less can be obtained by performing about [15 minute room] processing by rotational frequency 20000rpm.

[0030] In this invention, the method of passing an orifice under the conditions whose differential pressure of the entrance side of the method of carrying out the opposite collision of the approach using the high-pressure homogenizer which is the approach of a publication, i.e., said silica slurry, by the pressure of 300kg/cm² or more of processing pressure force, or an orifice, and an outlet side is 300kg/cm² or more is mentioned to JP,9-142827,A and a Japanese-Patent-Application-No. No. 366220 [11 to] official report as the still more suitable grinding approach.

[0031] The above-mentioned high-pressure homogenizer usually consists of the high-pressure generating section, the opposite collision section, or the orifice section which pressurizes a raw material slurry. As the high-pressure generating section, high pressure pumping currently generally called the plunger pump is adopted suitably. Moreover, there are various kinds of formats, such as a single string type, a 2 ream type, and a 3 ream type, in high pressure pumping, and any format can be especially adopted as it without a limit.

[0032] As equipment used in the above-mentioned approach, the equipment generally marketed as a high-pressure homogenizer can use it without limitation. If it illustrates concretely, a trade name nano mizer (nano mizer company make), a trade name Micro fluidizer (micro disk company make), trade name Altima IZA (SUGINO machine company make), etc. will be mentioned, for example.

[0033] Moreover, what is necessary is not to be restricted especially, either, and just to adjust suitably also about the processing conditions in the grinding approach using the above-mentioned high-pressure homogenizer, and the count of processing, so that the precipitate silicic acid specified by this invention can be obtained.

[0034] for example, the differential pressure of the entrance side by the side of the orifice in the case of making the processing pressure in the case of carrying out an opposite collision, and an orifice pass a silica slurry, and an outlet side -- both -- 1200kg/cm² or more is still more preferably desirable 800kg/cm² or more preferably 300kg/cm² or more.

[0035] Moreover, as for the collision rate of the silica slurry at the time of carrying out an opposite collision, it is desirable as a relative velocity that it is [second / second] 150m/second or more still more preferably 100m /or more preferably 50m /or more.

[0036] Although the linear velocity of the silica slurry at the time of passing an orifice does not generally have ***** in order to be dependent also on the aperture of the orifice to be used, it is desirable that it is [second / second] 150m/second or more still more preferably 100m /or more preferably 50m /or more as well as the above.

[0037] Moreover, the sequence of processing precipitate silicic acid by finishing agents, such as cationic resin mentioned above. The approach which is not restricted, for example, sprays and carries out surface treatment of liquefied or the finishing agent dissolved in the solvent to powder-like precipitate silicic acid 1 micrometer or less especially; in the solvent in which the finishing agent was dissolved. How to make dry and carry out surface treatment, after distributing powder-like precipitate silicic acid 1 micrometer or less; Precipitate silicic acid and a finishing agent are mixed to approach; or the solvent which carries out surface treatment at the same time a grinder grinds the mixture of solid-state-like precipitate silicic acid and a finishing agent. The approach of carrying out surface treatment etc. is

mentioned at the same time it grinds.

[0038] Also in it, if the dispersibility in the inside of rubber is taken into consideration, the approach of carrying out surface treatment is suitable at the same time it mixes and grinds precipitate silicic acid and a finishing agent to a solvent. Specifically, said silica slurry, and a finishing agent and the approach of mixing cationic resin preferably, and carrying out surface treatment of it with said high-pressure homogenizer, at the same time it grinds a finishing agent mixing silica slurry are suitable.

[0039] What is necessary is to be able to use the natural rubber latex usually used or the rubber latex of an emulsion-polymerization system that there is no limit in any way, and just to choose it suitably as a rubber latex used in this invention, according to the application made into the purpose. For example, if the tire engine performance is taken into consideration when using for a tire application, it is suitable to use the rubber latex of an SBR system.

[0040] In this invention, as an approach of mixing a rubber latex and precipitate silicic acid, if it mixes in the state of a solution, a well-known approach [be / no limit] can be used especially. What is necessary is generally, just to mix the rubber latex distributed by the oil emulsion, and a precipitate silicic acid water dispersion and the precipitate silicic acid water dispersion preferably ground with said high-pressure homogenizer.

[0041] In this invention, especially the compounding ratio of a rubber latex and precipitate silicic acid is not restricted, but can blend precipitate silicic acid by the conventional approach also by the high ratio which was not able to be attained. Usually, what is necessary is to take into consideration the precipitate silicic acid loadings in the precipitate silicic acid masterbatch mentioned later, and just to determine suitably.

[0042] What is necessary is just to use the approach which is not restricted especially about these processes, either and is generally used in the mixed liquor of the above-mentioned rubber latex and precipitate silicic acid although a precipitate silicic acid masterbatch can be obtained co-coagulation and by rinsing, dehydrating and drying in this invention.

[0043] For example, although the approach of adding salts, such as salt / the sulfuric-acid solidifying method, and making it solidify according to a salting out effect generally as an approach of carrying out co-coagulation is adopted, it is not limited to especially this approach, and if it solidifies when it mixes from the first, it is necessary not to dare add a salt.

[0044] Moreover, since it separates into the rubber solid content (henceforth crumb) and the moisture component (henceforth Ceram) of the latex usually solidified by carrying out co-coagulation as an approach of rinsing, dehydrating and drying After separating Ceram from the mixed liquor which carried out [above-mentioned] co-coagulation and obtaining crumb, the obtained crumb is rinsed in a tank etc. By squeezer etc., moisture is wrung and it dehydrates, and after a grinder etc. grinds finely, the method of obtaining a masterbatch is suitably adopted by fabricating in the shape of [which was dried with the hot blast type drier] a thing block.

[0045] What is necessary is not to restrict especially the amount of precipitate silicic acid in the precipitate silicic acid masterbatch obtained, but just to set it up suitably according to the purpose. For example, when using for a tire application, 20 - 40% of range is more preferably suitable 15 to 50% preferably.

[0046] The precipitate silicic acid masterbatch obtained by the approach of this invention can obtain the rubber which precipitate silicic acid fully distributed by the usual kneading approach.

[0047] Moreover, although it is dependent also on the property of the used precipitate silicic acid, the physical properties of the rubber obtained using the precipitate silicic acid masterbatch It compares with the precipitate silicic acid content rubber obtained by the approach of only carrying out melting ***** of the rubber currently performed conventionally and the precipitate silicic acid. The run bone wear used as the index of tire abrasiveness improves, the inclination of $\tan \delta$ of 0 degree C and 60 degrees C used as the index of wet grip nature will also become quite sudden, and its wet grip nature will also improve.

[0048]

[Example] Although an example and the example of a comparison are hung up over below in order to

explain this invention to a detail further, this invention is not limited to these examples. In addition, the physical properties in the following examples and examples of a comparison were measured by the following approach.

(1) Using the particle-size-distribution measuring device (the product made from coal tar, coal tar LS-230) of a mean-particle-diameter light-scattering diffraction type, the volume criteria median diameter was measured and this value was adopted as mean particle diameter.

[0049] In addition, on the occasion of measurement, the refractive index 1.332 of water (dispersion medium) and the refractive index 1.458 of precipitate silicic acid were inputted as a parameter.

(2) Use a Mooney viscosity Mooney viscometer (made in the Kamishima factory: VR-103ST), and measure at 100 degrees C. It is shown that workability is so good that a value is small.

(3) Degree of hardness JIS According to K6301, it measured with the JIS-A hardness meter.

(4) 300% modulus JIS It measures by the tensile-stress examining method of K6301.

(5) Tensile strength JIS It measures by the tensile strength examining method of K6301.

(6) Elongation JIS It measures by the elongation examining method of K6301.

(7) It measured using the exoergic good rich flexometer.

(8) Impact resilience JIS The impact resilience of K6301 is measured at 30 degrees C.

Commercial 976ml (silica concentration: 28.19%, mole-ratio:3.04) of specific silicate water solutions, 692ml (sodium-oxide concentration: 10%) of sodium-sulfate water solutions, and 4426ml of water were thrown in using the reaction container made from stainless steel of 110l. of examples. In order to make a neutralization index 50% after making this solution into 35 degrees C, 331ml of sulfuric acids of 22.34 weight / volume % was thrown in. Then, the temperature up of the solution temperature was carried out to 95 degrees C, and it agitated for 5 minutes in the condition as it is. Subsequently, the sulfuric acid of previous concentration was thrown in for 331ml over 50 minutes. Finally, PH of reaction mixture was stirred until it was set to 5.2, and the precipitate silicic acid slurry was obtained.

[0050] At this time, the specific surface area of the obtained precipitate silicic acid was 276m²/g, and oil absorption was 250 cc / 100g.

[0051] Once distributing by the disperser so that precipitate silicic acid concentration may become 15% using this precipitate silicic acid slurry, as cationic resin, the diaryl dimethylammoniumchloride-acrylamide copolymerization object (trade name PAS-M -1, Nitto Boseki Co., Ltd. make) water solution was added, and mixed liquor was obtained so that it might be set to 20phrs to the amount of precipitate silicic acid. After carrying out preliminary mixing of this mixed liquor by the mixer, by performing processing 3 times by 400kg/cm² of processing pressure force using a high-pressure homogenizer, grinding and surface preparation were performed to coincidence and the cationic resin surface-preparation precipitate silicic acid water solution was obtained. The mean particle diameter of the obtained precipitate silicic acid was 620nm.

[0052] Subsequently, after mixing the 600 cc of the above-mentioned cationic resin surface treatment precipitate silicic acid water solutions, and SBR rubber-latex (solid-content concentration: 20%) 1000cc which adjusted precipitate silicic acid concentration to 12% and fully stirring, 200 cc of NaCl water solutions was added 10%, and co-coagulation was carried out. After filtering and rinsing this co-coagulated substance, it dried and the precipitate silicic acid masterbatch was obtained. The rate of combination of precipitate silicic acid was about 35%.

[0053] The rubber physical properties when kneading and measuring by the 6 inch mixer using the obtained precipitate silicic acid masterbatch are shown in Table 1.

Commercial specific silicate solution (silica concentration: 27.11%, mole-ratio:3.23) 51.1L and water 243L were supplied using the reaction container made from stainless steel of 3 21m of examples. In order to make a neutralization index 50% after making this solution into 35 degrees C, the 15.16L injection of the sulfuric acid of 22.11 weight / volume % was done. Then, the temperature up of the solution temperature was carried out to 95 degrees C, and it agitated for 5 minutes in the condition as it is. Subsequently, the sulfuric acid of previous concentration was thrown in for 14.89L over 45 minutes. Finally PH of reaction mixture was stirred to 4.2, and the precipitate silicic acid slurry was obtained.

[0054] At this time, the specific surface area of the obtained precipitate silicic acid was 189m²/g, and oil

absorption was 210 cc / 100g.

[0055] Once distributing by the disperser so that precipitate silicic acid concentration may become 11% using this precipitate silicic acid slurry, as cation resin, the diaryl dimethylammoniumchloride-acrylamide copolymerization object (trade name PAS-M -1, Nitto Boseki Co., Ltd. make) water solution was added, and mixed liquor was obtained so that it might be set to 8phrs to the amount of precipitate silicic acid. After carrying out preliminary mixing of this mixed liquor by the mixer, by performing processing once by 800kg/cm² of processing pressure force using a high-pressure homogenizer, grinding and surface preparation were performed to coincidence and the cation resin surface-preparation precipitate silicic acid solution was obtained. The mean particle diameter at this time was 320nm.

[0056] Using the above-mentioned cation resin surface-preparation precipitate silicic acid solution, the same actuation as an example 1 was performed, and the precipitate silicic acid masterbatch was obtained. The rate of combination of precipitate silicic acid was about 35%.

[0057] The rubber physical properties when kneading and measuring by the 6 inch mixer using the obtained precipitate silicic acid masterbatch are shown in Table 1.

It distributed by the disperser using the precipitate silicic acid slurry adjusted by the same reaction condition as example of comparison 1 example 1, without adding cationic resin. The mean particle diameter in the solution at this time was 16.3 micrometers.

[0058] Although the same actuation as an example 1 was performed using the precipitate silicic acid of the above-mentioned distributed condition, it flowed out at the time of rinsing, and most precipitate silicic acid was not incorporated in rubber.

[0059]

[Table 1]

表1

項目	単位	実施例1	実施例2	比較例1
ムーニー粘度	—	68.9	51.1	混練せず
硬度	—	71	58	
300%モジュラス	kg/cm ²	68	55	
引張強度	kg/cm ²	254	232	
伸び	%	780	690	
発熱	℃	79	73	
反発弾性	%	17.1	15.2	

[Effect of the Invention] The precipitate silicic acid masterbatch obtained by this invention is reduction of the production cost by compaction of - kneading time amount, and improvement in productivity.

- Prevention of contamination by scattering at the time of precipitate silicic acid kneading.
- Amelioration of the rubber physical properties by improvement in the dispersibility of precipitate silicic acid.
- It has the advantage of improvement in the degree of freedom of a precipitate silicic acid design.

[0060] The precipitate silicic acid masterbatch obtained by this invention has various advantages which were described above, and when it manufactures various kinds of rubber goods using this masterbatch, it demonstrates the outstanding effectiveness it is ineffective to the former.

[Translation done.]